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(54) Title: METHOD FOR INHIBITING METAL CORROSION IN LARGE SCALE WATER SYSTEMS		
(57) Abstract <p>A method inhibiting metal corrosion in a closed water system such as is found in industrial, commercial and institutional systems which utilizes a formulation comprising at least one water soluble fatty acid salt of the formulae $R\text{COOX}$ and $R^1(\text{COOX})_n$ wherein R is alkyl C₆₋₁₈, or hydroxyalkyl (6-18), R¹ is alkyl C₂₋₁₈ or hydroxyalkyl C₂₋₁₈, X is a salt forming cation and n is 2 or 3. The corrosion inhibiting salt(s) is present in an amount 1 to 1000 parts per million parts of the aqueous treatment system. Other additives for helping to reduce corrosion of metal such as benzoates, silicates, nitrates, molybdates, triazole and the like may also be present.</p>		

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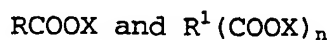
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**Method For Inhibiting Metal Corrosion
In Large Scale Water Systems**

5 This invention relates to a method for inhibit-
ing metal corrosion in a closed water system such as is
found in industrial, commercial or institutional systems,
including without limitation HVAC systems of hospitals,
universities, office towers, factories, shopping malls and
10 the like. More particularly, the invention relates to a
method for inhibiting metal corrosion in such a system by
maintaining therein an effective amount of at least one
water soluble fatty acid salt as hereinafter more particu-
larly defined. The invention further relates to certain
15 corrosion inhibiting compositions, the aqueous
formulations containing the same and the systems produced
therefrom by dilution with water.

 The corrosion inhibiting formulations for use in
the aforesaid closed water systems comprise at least one
20 water soluble fatty acid salt selected from salts having
the formulae



25 wherein R is straight or branched chain alkyl having at
least 6 carbon atoms and preferably 6 to 18 carbon atoms
or hydroxyalkyl having at least 6 and preferably 6 to 18
carbon atoms, X is a cation (ammonium, alkali metal, amine
or any other basic compound which forms a salt with said
30 fatty acid), R^1 is alkyl or hydroxyalkyl having at least 2
carbon atoms, and preferably 2 to 18 carbon atoms and n is
2 or 3 and optionally at least one additive selected from
the group of alkali metal borates, alkali metal
molybdates, hydrocarbyl triazoles, silicates and amines

such as ethylenediamine, morpholine, pyridine and pyrrolidine.

5 The corrosion inhibiting compositions of the invention, in addition to their effectiveness for their intended purpose are also environmentally acceptable because of their low toxicity and reduced adverse effect when discharged into a waste stream. While a variety of corrosion inhibitors have been proposed, many of the conventional corrosion inhibitors have themselves been
10 found to cause problems when employed in corrosion inhibiting formulations. For example phosphate compounds have been found to be good corrosion inhibitors but attendant problems may result from the use of phosphate compounds. For example, the dilution of a corrosion inhibiting
15 formulation containing phosphate corrosion inhibitors with hard water will cause the precipitation of insoluble alkali earth phosphate salts from the aqueous corrosion inhibiting aqueous solutions. The precipitation causes rapid depletion of the phosphate in solution and in turn
20 causes a decrease in corrosion protection. In addition, the precipitating solids will scale and eventually have detrimental effects on the system. The use of various anti-precipitation additives in phosphate containing anti-corrosion formulations has been proposed, however, the
25 uses of such additives increases the overall cost of the formulation. In addition, several governmental authorities have banned the use of phosphates in aqueous systems because of their detrimental effects to the environment when the water in the system has to be discharged. Other
30 conventional corrosion inhibitors have problems associated with their use in aqueous corrosion inhibiting systems, as for example, the amine and nitrite compounds which are often employed as corrosion inhibitors may form dangerous

nitroso compounds particularly when they are used together.

It would therefore be advantageous to develop a metal corrosion inhibiting formulation for use in a closed water system which provides adequate protection for a variety of metals without requiring the use of organophosphates, amines and/or nitrites or heavy metal compounds such as chromates and molybdates.

Special requirements and considerations come into play in treating such large scale closed water systems. There are significant differences between such systems and for example automobile cooling systems, other internal combustion engine systems, boilers and the like which have been well documented.

Closed systems are constituted of a water filled closed loop, typically constructed of steel pipes in which there is minimal air contact with the water in the system.

Air contact, however, can and does occur as for example if the system has a sump open to the air. The corrosion inhibitor(s) employed therefore have to be stable against decomposition and/or oxidation and above all are required to be effective to prevent oxidation of metal i.e., corrosion. The metal of most concern is typically mild steel although corrosion protection for brass, solder, copper, cast iron, aluminum, magnesium and their alloys is also important as components of the systems such as valves, heat exchangers, etc. are constructed from these metals.

Another major factor to be considered in connection with water treatment for large scale closed systems as contemplated herein is that these systems, many times, sit with uncirculated water for prolonged periods i.e., for months, when the system for example a heating system is shut down in the hot summer months and a cool-

ing/chiller system is shut down for the cold winter months. The non-circulating water during these time periods remains stagnant. The corrosion inhibitor employed must be effective both in a flowing and in a non-flowing or static condition.

Still another area of concern for closed system water treatment is that the corrosion inhibitor used for example, in a building's hot water heating system and/or air conditioning chiller system must be stable in performance for prolonged periods of time, by which is meant years. It is most desirable to treat the system once and for the system to require minimal additional treatment or monitoring over this extended period. Systems of the type contemplated herein are frequently very complicated in construction and can contain miles of steel pipe, for example when installed in a large building complex. Leaks and water losses do occur. These leaks in turn reduce the amount of corrosion inhibitor in the system. Such leaks of the treated water in the system which took place heretofore and when the heretofore available corrosion inhibiting agents such as chromates and hydrazine were utilized, gave rise to health concerns because of the recognized toxicity of these materials and because they are suspected of being carcinogens.

Alkali metal molybdate based formulations have also been proposed for use in closed aqueous systems and have been found to be effective as corrosion inhibitors. Even though such molybdates are much less toxic than the chromates and hydrazine, many communities have imposed waste discharge limits with respect thereto as molybdenum is perceived and is classified as a toxic heavy metal.

Nitrites and borate-nitrites have heretofore been employed as corrosion inhibitors in closed systems

and particularly have been used together with amine compounds. Their use is characterized by a relatively high inorganic solids content which gives rise to a solids buildup in the case where a leak has occurred. Such solids can cause caustic crevice corrosion at fitting connections and also on the external surfaces of the equipment as they usually are highly alkaline. The use of nitrites is furthermore undesirable as they are microbiological nutrients and their discharge can cause eutrophication. Treatment solutions containing nitrites are frequently unstable in use as there are microorganisms present in the system which consume the nitrites decreasing or eliminating the corrosion inhibitor from the system.

The heretofore conventional use of phosphorus containing compounds in the formulations is also undesirable as such compounds support microbiological growth in as much as they constitute an essential nutrient for microorganisms. The proposed use of organophosphorus compounds has also been found to be undesirable as the organophosphorus compounds eventually convert to phosphate which in turn gives rise to precipitates of insoluble alkaline earth metal phosphate salts by reaction with the soluble calcium present in the water. This precipitation causes rapid depletion of the phosphate in the treatment solution resulting in a decrease in corrosion protection.

In addition, the precipitating solids will scale and eventually plug the passages of the system. This is the case with the use of many of the organic phosphonates such as hydroxyphosphonoacetic acid (HPA), 1-hydroxyethylidene-1,1-diphosphonic acid (HEDPA) or 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) and other organophosphonates.

Prior Art

U.S. Patent No. 4,759,864 describes the use of C₆-C₁₂ aliphatic monobasic acids or their alkali metal salts in automotive antifreeze formulations.

5 U.S. Patent No. 5,269,956 is directed to corrosion inhibiting compositions including potassium, an aliphatic monocarboxylate having at least 5 carbon atoms, hydrocarbyl triazole and one or more of the group of silicates, phosphates or borates useful in heat transfer
10 fluids, antifreezes and for corrosion inhibition in motor vehicle engines.

In U.S. Patent No 4,851,145 the combination of alkylbenzoic acid with monobasic and dibasic fatty acids is disclosed for use in corrosion inhibiting antifreeze
15 formulations. Canadian Patent No. 1,118,990 describes corrosion inhibitors for closed water systems comprising at least one molybdate and at least one amine such as morpholine and ethylenediamine. There may also be present a supplementary inhibitor such as benzotriazole,
20 sodium polymethacrylate or a copolymer of a sulphonatated polystyrene and malic anhydride.

Canadian Patent No. 1,116,026 relates to inherently bactericidal metal working fluids having corrosion inhibiting activity composed of boric acid, an alkali
25 tetraborate, an alkanol amine, pelargonic acid, a non-ionic surfactant and water. The compositions are metal working fluids and for this application must be used in such high concentration as would render them unsuitable for large scale closed water treatment systems.

30 Several of the above-noted references disclose the use of monobasic fatty acids and dibasicarboxylic acids. The sole reference directed to closed water systems (Canadian Patent 1,118,990) however does not, but

rather teaches the use of a combination of molybdate and amine as a corrosion inhibitor for closed water systems. The references dealing with fatty acid and dicarboxylic acid use teach their use in automotive antifreezes and metal-working fluids where they are used in much higher concentrations than that taught herein.

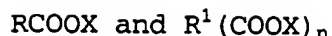
Water treatment for closed water systems has different requirements as compared to water treatment applicable to automotive internal combustion engines or metal working or antifreeze applications and the common practices of the latter are not applicable to the former.¹

It is the object of the instant invention to provide a corrosion inhibiting concentrate formulation for closed water systems, an aqueous corrosion inhibiting system produced therefrom by dilution with water which contains no phosphates, molybdates, chromates, hydrazine, high solids content, nitrites, etc., yet which remains effective in preventing corrosion of a variety of metals in both static and active, i.e., flowing liquid conditions and to provide a method for corrosion protection for various metals and processes involving industrial, commercial and institutional closed water systems which avoids the disadvantages of the heretofore available methods.

Summary of the Invention

The present invention is directed to a method for inhibiting metal corrosion in a closed water treatment system by supplying to and maintaining therein an effective amount of at least one water soluble fatty acid salt selected from salts having the formulae

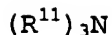
¹ The NALCO Water Handbook, sec. ed. McGraw-Hill 1988, Chapter 37, pp. 37.1-37.13. Betz Handbook of Industrial Water Conditioning, 7th ed., 1976, Chapter 26, pp. 185-191 and pp. 223-225.



wherein R is straight or branched chain alkyl having at least 6 carbon atoms and preferably 6 to 18 carbon atoms or hydroxyalkyl having at least 6 and preferable 6 to 18 atoms, X is a cation such as ammonium, alkali metal, amine or any other basic compound which forms a salt with the fatty acid, R^1 is alkyl or hydroxyalkyl having at least 2 carbon atoms and preferably 2 to 18 carbon atoms and n is 2 or 3 and optionally at least one additive which may be a corrosion inhibitor, selected from the group of alkali metal borates, alkali metal molybdates, hydrocarbyl triazoles, silicates, morpholine, ethylenediamine, pyridine and pyrrolidine.

Typical straight chain alkyl groups are hexyl, octyl, decyl, nonyl dodecyl, hexadecyl and octadecyl. Examples of branched chain alkyl groups include ethylhexyl, trimethylhexyl, and ethylnonyl. The hydroxy alkyl groups are analogous to the aforementioned alkyl groups except for the presence of the hydroxy groups. While monohydroxyalkyl groups predominate, dihydroxyalkyl groups such as in malic acid and tartaric acid and trihydroxyalkyl groups are equally suitable. Mixtures of two or more of the salts of the various acids can also be used.

The acids are used in the form of their water soluble salts i.e., X in the formulae is a salt forming cation. Illustrative salts are the sodium, potassium, lithium, ammonium and amine salts. Particularly useful salts include the alkali metal, ammonium, alkylolammonium (e.g. monoethanol ammonium or triethanol ammonium salts). When X is an amine, it corresponds to the formula



wherein each R^{11} is independently hydrogen, C_{1-10} alkyl or
5 C_{2-10} hydroxyalkyl. When each of R^{11} is hydrogen, the
cation is ammonium. $(R^{11})_3N$ can also be a primary,
secondary or tertiary monoamine. In some instances at
least one of R^{11} is di- or tri-(hydroxyalkyl) and $(R^{11})_3N$ is
10 then for example diethanolamino, diethylaminoethanol or
triethanolamino. (R^{11}) can also be designate an alicyclic
group as for example cyclohexylamino, cyclopropylamino,
and cyclopentylamino. $(R^{11})_3N$ can also represent a
heterocyclic group as for example morpholino, pyridino,
pyrrolidino and the like.

15 The salts of dicarboxylic and tricarboxylic
acids which are used in formulating the corrosion
inhibitors of the present invention are represented by the
formula $R^1(COOX)_n$, wherein X has the meaning as set forth
above and R^{11} is straight or branched chain alkyl having 2
20 or more carbon atoms and preferably not more than 18
carbon atoms. Illustrative examples of straight chain
alkyl are ethyl, propyl, butyl, pentyl, hexyl, octyl,
monyl, decyl, undecyl, dodecyl, hexadecyl and octadecyl
and of the branched chain alkyl are ethylhexyl,
25 trimethylhexyl, and the like. Illustrative of
hydroxyalkyl groups are hydroxyethyl, hydroxypropyl,
hydroxyhexyl and the like.

Illustrative instances of acids preferred for
use herein include: valeric, caproic, caprylic, capric,
30 pelargonic, heptanoic, octanoic, isovaleric, 2-ethyl-
hexanoic, nonanoic, sebacic, dodecanedioic, neodecanoic,
succinic, undecanedioic, isononanoic, trialkylacetic,

tartaric acid, palmitic, stearic, malic, citric, malonic, glutaric and adipic, and the like.

5 The corrosion inhibiting compositions of the invention are water soluble and can be used in the form of aqueous compositions including therein a substantial percentage of water. More particularly, they can be utilized per se or in the form of concentrates to be diluted with water on site.

10 In accordance with the invention the aqueous system has incorporated therein a corrosion inhibiting amount of at least one of the above described monocarboxylic and/or dicarboxylic acid salts. A corrosion inhibiting amount preferably is from about 1 part to about 1000 parts of corrosion inhibitor per million parts of the aqueous treatment system, more preferably about 50 parts
15 to about 500 parts and most preferably about 300 parts of corrosion inhibitor per million parts of the aqueous treatment system.

20 The aqueous systems of the present invention also can contain other additives, singly or in combination to help reduce corrosion, and include additives such as alkali metal hydroxides, benzoates, silicates, nitrates, molybdates, hydrocarbyl triazoles and the like.

25 The triazole component may be any hydrocarbyl triazole such as tolyltriazole 2-methylbenzotriazole, mercaptobenzotriazole and benzotriazole.

30 The borate can be a tetraborate such as sodium tetraborate, also known as borax, potassium tetraborate and mixtures thereof, boric acid, or an alkali metal borate such as potassium borate.

The silicate component must be water soluble and may be one or mixtures of the following: sodium-metasilicate pentahydrate, sodium-metasilicate

nonahydrate, sodium orthosilicate pentahydrate, anhydrous sodium silicate and the like.

The nitrate component typically is an alkali metal nitrate such as potassium nitrate.

5 The molybdate is also typically an alkali metal molybdate such as sodium molybdate.

In addition, different anti-scaling and dispersing polymers, copolymers, terpolymers and tetramers of acrylic acid may be present in the aqueous treatment
10 solution. Illustrative of the monomer groups which can be present are those derived from maleic anhydride, sulphonated styrene, AMPS, polymethacrylate(s) and hydrolyzed polyacrylamides. This type of additive is well known to the art for their ability to:

15 (1) inhibit, retard or prevent objectionable scale formation on high temperature heat exchange surfaces, as would be likely to occur in hot water heating systems using unsoftened make-up water, and

20 (2) retard crystal growth of calcium, magnesium and iron deposits. Such crystalline deposits are particularly detrimental to the performance of pump seals and heat exchange surfaces.

The polymers or copolymers are water soluble and include without limitation the water soluble salts of
25 copolymers of acrylic acid and maleic acid including for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials and are described in European Patent Application No. 66915 published Dec.1,
30 1982.

Other conventional additives may additionally be present such as nitrite, borate - nitrite, chromate, amines, hydrazine, phosphate and phosphonate compounds,

however their inclusion may not be desirable for the reasons noted earlier.

5 The optional components generally represent less than about 200 ppm, preferably about 15 to about 100 ppm of the components introduced into the closed water treatment system and in the concentrate, from about 1 to about 40%, preferably 5 to 20% by weight of the other non aqueous components.

10 The preferred composition for the method of the invention comprises:

(a) from about 1 to about 30% by weight of at least one of the water soluble monocarboxylic acids $R\text{COOX}$ and water soluble dicarboxylic acids $R^1(\text{COOX})_n$ wherein R , R^1 , n and X are as previously defined.

15 (b) from 0% to about 40% by weight of at least one of alkali metal hydroxides, benzoates, silicates, nitrates, molybdates, hydrocarbyl triazoles, acrylic polymers and copolymers,

(c) the balance of the composition comprising water

20 The method of the invention is practiced by introducing into the water of a closed system such as the HVAC system of a building complex and maintaining therein an amount of the composition effective to inhibit corrosion of metal in that water environment. The materials
25 are either mixed together and added to the water or are mixed together and added to a relatively small amount of water to form a concentrate which is then added to the water in the system.

30 The following examples more fully describe the corrosion inhibitor compositions the invention and illustrate how they are used. These examples are merely illustrative of the invention and should not be construed as limiting in any way the scope thereof.

EXAMPLE 1: STATIC SOLUTION CORROSION TESTS (TABLES 1 TO 4)

The water used was tap water from Lake Ontario.

5 All tests contained a buffering amount of the amine morpholine or sodium metaborate. These tests were all initially at a pH of about pH 9.4. The beakers were open to air and any liquid loss was made up with deionized water so that no additional salts were introduced. Metal test coupons were submerged and allowed to sit in this treated tap water in open beakers at room temperature for approximately one month at which time the submerged metal coupons were removed and the corrosion rate was determined and expressed as metal loss penetration in thousandths of inches (mils) per year (MPY). ASTM procedure D2688-90 was followed in the preparation, processing and MPY

10 determinations of the metal coupon test pieces. All of the metal test pieces were of the same size and dimensions and of the same metallurgy. ASTM 1010 mild steel was used. The lower the MPY value achieved the more successful the corrosion inhibitor. Realizing a low corrosion rate is most desirable for the mild steel test piece because closed systems are primarily constructed using this grade of steel for the piping. The corrosion rate was also tested using aluminum and copper as corrosion of these metals is also an issue in closed systems.

25 All of the monocarboxylic, dicarboxylic and tricarboxylic acid materials used were neutralized with the appropriate amount of sodium or potassium hydroxide to obtain a neutralized salt in solution. Morpholine or sodium metaborate was then added to obtain a pH of 9.4 which was the standard test pH and used for all the tests.

30

Maintaining the same pH for all of the tests is important as it is well known that the pH of an aqueous solution

significantly affects the corrosivity to metals especially in the case of mild steel.

Table 1 shows the results of static beaker corrosion tests which contained the recited level of ingredients and which included linear C₆, C₈, and C₁₀ fatty acid. (caproic, caprylic and capric) and other inhibitors as indicated.

Table 1 also provides the corrosion values obtained with the known morpholine plus sodium molybdate based inhibitor treated water and of morpholine alone. 225 ppm morpholine was used in the test as this was the quantity required to obtain a pH of 9.4 in this test protocol. If the tap water was left at its normal pH of 7.5, the mild steel corrosion rate would be approximately 10 MPY over this time period, A corrosion rate of less than 1 MPY on the steel piece is most desirable.

The mixture of caproic, caprylic, capric acid (C₆, C₈, C₁₀ respectively) was used as it is a readily available material.

From Table 1, it can be appreciated that corrosion inhibition on the mild steel and the aluminum test coupons is realized with an increasing concentration of these fatty acids. An effective total dosage of between 50 and 345 ppm of these fatty acids gives excellent corrosion inhibition on steel and aluminum at the described static conditions. As mentioned previously, obtaining corrosion inhibition at static (no flow) conditions is extremely desirable and is difficult to obtain with many other corrosion inhibitors.

TABLE 1: STATIC CORROSION INHIBITION USING WATER SOLUBLE
FATTY ACID SALTS

TEST #	CONCENTRATION OF COMPO- NENTS	MPY ON MILD STEEL	MPY ON ALU- MINUM	MPY CORRO- SION RATE ON COPPER
1	225 ppm morpholine	4.3	n.t.**	0.33
2	1.5 ppm caproic acid 28 ppm caprylic acid 20 ppm capric acid 225 ppm morpholine 15 ppm tolyltriazole	2.5	1.3	0.05
3	3 ppm caproic acid 56 ppm caprylic acid 40 ppm capric acid 270 ppm morpholine 15 ppm tolyltriazole	<0.03	1.4	<0.02
4	6 ppm caproic acid 112 ppm caprylic acid 80 ppm capric acid 300 ppm morpholine 15 ppm tolyltriazole	<0.03	0.55	<0.02
5	10 ppm caproic acid 193 ppm caprylic acid 224 ppm capric acid 300 ppm morpholine 15 ppm tolyltriazole	<0.03	0.3	<0.02
6	300 ppm morpholine 195 ppm sodium molyb- date dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) 15 ppm tolyltriazole	0.14	0.01	n.t.

5

** n.t. not tested

Table 2 describes tests carried out with the water adjusted to pH 9.4 with sodium metaborate. This was done to establish if this practical buffering method had any significant effect on corrosion rates when using fatty acids. The corrosion inhibition by the C₈ and C₁₀ fatty acid mix is slightly inferior in the sodium metaborate pH adjusted solutions compared to the morpholine pH adjusted solutions. Example 11 establishes that citric acid, a tricarboxylic acid, is an effective corrosion inhibitor for mild steel. It is to be noted that increased corrosion inhibition could be realized by increasing the fatty acid salt concentration.

**TABLE 2: STATIC CORROSION INHIBITION WITH WATER SOLUBLE
FATTY ACID SALTS**

TEST #	CONCENTRATION OF COM- PONENTS	MPY ON MILD STEEL	MPY ON ALU- MINUM	MPY CORRO- SION RATE ON COPPER
7	1.5 ppm caproic acid 28 ppm caprylic acid 20 ppm capric acid 180 ppm $\text{Na}_2\text{B}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ 15 ppm tolyltriazole	3.3	1.8	0.04
8	3 ppm caproic acid 56 ppm caprylic acid 40 ppm capric acid 210 ppm $\text{Na}_2\text{B}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ 15 ppm tolyltriazole	0.08	1.4	<0.02
9	6 ppm caproic acid 112 ppm caprylic acid 80 ppm capric acid 210 ppm $\text{Na}_2\text{B}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ 15 ppm tolyltriazole	<0.03	0.7	<0.02
10	10 ppm caproic acid 193 ppm caprylic acid 224 ppm capric acid 210 ppm $\text{Na}_2\text{B}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ 15 ppm tolyltriazole	<0.03	0.7	<0.02
11	345 ppm citric acid 210 ppm $\text{Na}_2\text{B}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ 15 ppm tolyltriazole	0.18	n.t.	n.t.

TABLE 3 shows the corrosion inhibiting properties of various concentrations of various other monocarboxylic fatty acids using the same static conditions described in Table 1. Table 3 demonstrates the efficacy of these various fatty acids. The fatty acid concentration in all of these tests was 345 parts per million.

Comparing the data in Tables 1 to 3, it can be seen that some fatty acids are more effective than others.

In general, the trend indicates a longer fatty acid carbon chain yields more effective steel and aluminum corrosion inhibition.

TABLE 3

TEST #	CONCENTRATION OF COMPONENTS	MPY ON MILD STEEL	MPY ON ALUMI-NUM	MPY CORROSION RATE ON COP-PER
12	345 ppm pelargonic acid 300 ppm morpholine 15 ppm tolyltriazole	0.02	0.3	0.02
13	345 ppm heptanoic acid 300 ppm morpholine 15 ppm tolyltriazole	1.7	0.96	<0.02
14	345 ppm isovaleric acid 300 ppm morpholine 15 ppm tolyltriazole	3.3	0.89	<0.02
15	345 ppm isononanoic acid 300 ppm morpholine 15 ppm tolyltriazole	1.67	1.0	<0.02

Table 4 sets forth the corrosion rates obtained using various pure dicarboxylic acids, commercially available mixtures of dicarboxylic acids and mixtures of dicarboxylates and monocarboxylates. A comparative 345 ppm concentration of the mixed and pure dicarboxylic acid

and of the mixtures of various mono dicarboxylic acids was used.

5 A commercially available mixture of, primarily, three dicarboxylic acids, comprising 36% dodecanedioic acid 41% undecanedioic acids, 7% sebacic acid and 13% other dibasic acids was employed in the test reported in Table 4. From the data in Table 4, it can be seen that this combination of dicarboxylic acids is an extremely effective static corrosion inhibitor for steel at a relatively low concentration and is synergistic in its performance compared to various pure dicarboxylic and monocarboxylic acids.

10 From the data reported in Tables 3 and 4, it can also be appreciated that there is an unexpected synergistic corrosion inhibition when sebacic acid and isononanoic acid (3,5, 5-trimethylhexanoic acid) are combined.

20 Very desirable static corrosion inhibition is also seen when mixtures of sebacic acid and commercially available trialkyl acetic acids in which each hydrogen of the acetic acid has been replaced by an alkyl group were tried. The resulting quaternary alpha carbons of these acids and all of their derivatives are reported to have a much higher thermal, oxidative and hydrolytic stability compared to the linear fatty acids. The combination used in Test #21 mixture of neodecanoic acids with, primarily, 10 carbon atoms. The acids used in Text #20 a mixture of acids having from 9 to 13 carbon atoms.

25 Tests 22 and 23 utilized 50 and 100 ppm tartaric acid concentrations respectively. The salt of this dicarboxylic acid is also a very good static corrosion inhibitor especially at the higher 100 ppm concentration.

TABLE 4

TEST #	CONCENTRATION OF COMPONENTS	MPY ON MILD STEEL	MPY ON ALUMI-NUM	MPY CORROSION RATE ON COPPER
16	345 ppm sebacic acid 300 ppm morpholine 15 ppm tolyltriazole	2.8	3.3	<0.02
17	100 ppm dodecanedioic acid 270 ppm morpholine 15 ppm tolyltriazole	2.4	n.t.	n.t.
18	100 ppm acid mixture* 270 ppm morpholine 15 ppm tolyltriazole	<0.02	n.t.	n.t.
19	100 ppm sebacic acid 245 ppm isononanoic acid 300 ppm morpholine 15 ppm tolyltriazole	0.02	0.67	<0.02
20	261 ppm acid mixture** 84 ppm sebacic acid 300 ppm morpholine 15 ppm tolyltriazole	<0.02	n.t.	n.t.
21	261 ppm acid mixture*** 84 ppm sebacic acid 300 ppm morpholine 15 ppm tolyltriazole	<0.02	n.t.	n.t.
22	50 ppm tartaric acid 300 ppm morpholine 15 ppm tolyltriazole	3.1	0.65	0.02
23	100 ppm tartaric acid 300 ppm morpholine 15 ppm tolyltriazole	0.3	0.53	<0.02

* Mixture of dodecanedioic, undecanedioic and sebacic acids.

** Mixture of neodecanedioic acids having from 9 to 13 carbon atoms.

*** Mixture of neodecanedioic acids having primarily 10 carbon atoms.

EXAMPLE 2: HOT WATER TEST RIG

It is very desirable for the closed system treatment to be able to maintain its efficacy at elevated water temperatures of up to 100° celsius. Test evaluations

5 at a water temperature of 80° celsius were carried out to investigate the carboxylic acid compound(s) performance at this water temperature. The tests were carried out on a small seven liter internal volume recirculating system loop which was constructed from 1 inch internal diameter
10 ASTM 316 stainless steel piping. Lake Ontario tap water was always used as the water source. This hot water was recirculated across the metal test pieces at one foot per second velocity. The hot water temperature was achieved by flowing the water across a stainless steel immersion
15 heater, which had its heating capacity controlled using a rheostat. The metal test pieces and the MPY determinations were carried out as described in Example 1.

The test exposure period for the metal test pieces was approximately three days.

20 Tables 5 and 6 set out the test results using various water treatments and concentrations of the mono- and dicarboxylic acids and mixtures of these acids using the hot water test rig described above. Tests conducted utilizing the above described hot water test rig and using
25 untreated Lake Ontario water yielded a mild steel corrosion rate of greater than 20 MPY on the standard test pieces. Treatment yielding less than one MPY on the steel piece are desirable.

30 As set forth with respect to Example 1, the carboxylic acids are neutralized with the appropriate amount of sodium or potassium hydroxide to yield a neutral

solution pH and then the appropriate amount of morpholine or metaborate is added to obtain a final solution pH of 9.4 at room temperature.

5 Test 24 shows the corrosion rate obtained on this test rig using a known, existing commercial closed system formulation.

10 From the results in Tables 5 and 6 it appears obvious that many dicarboxylic and monocarboxylic acids and their mixtures are effective steel corrosion inhibitors in a closed system.

TABLE 5: HOT WATER TEST RIG RESULTS

TEST #	CONCENTRATION OF COMPONENTS	MPY ON MILD STEEL	MPY ON ALUMINUM	MPY CORROSION RATE ON COPPER
24	150 ppm morpholine 105 ppm $\text{Na}_2\text{B}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ 195 ppm $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ 9 ppm tolyltriazole	0.6	44	0.15
25	51 ppm tartaric acid 300 ppm morpholine 15 ppm tolyltriazole	0.3	76	<0.15
26	300 ppm morpholine 204 ppm tartaric acid 15 ppm tolyltriazole	<0.1	14	<0.15
27	100 ppm tartaric acid 10 ppm caproic acid 193 ppm caprylic acid 224 ppm capric acid 300 ppm morpholine 15 ppm tolyltriazole	<0.1	44	n.t.
28	10 ppm caproic acid 193 ppm caprylic acid 224 ppm capric acid 300 ppm morpholine 15 ppm tolyltriazole	0.6	52	0.15
29	6 ppm caproic acid 113 ppm caprylic acid 80 ppm capric acid 300 ppm morpholine 15 ppm tolyltriazole	0.6	4.4	n.t

TABLE 6: HOT WATER TEST RIG RESULTS

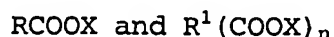
TEST #	CONCENTRATION OF COMPONENTS	MPY ON MILD STEEL	MPY ON ALU-MINUM	MPY CORROSION RATE ON COPPER
30	270 ppm morpholine 200 ppm acid mixture* 15 ppm tolyltriazole	0.2	23	0.18
31	300 ppm morpholine 100 ppm isononanoic acid 100 ppm acid mixture* 15 ppm tolyltriazole	2.0	22	0.18
32	216 ppm $\text{Na}_2\text{B}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ 204 acid mixture* 15 ppm tolyltriazole	0.2	42	<0.15
33	270 ppm morpholine 102 ppm acid mixture* 15 ppm tolyltriazole	1.9	18	<0.15
34	108 ppm $\text{Na}_2\text{B}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ 102 ppm acid mixture* 15 ppm tolyltriazole	0.8	18	0.21
35	300 ppm morpholine 345 ppm acid mixture* 15 ppm tolyltriazole	0.1	20	<0.15
36	210 ppm $\text{Na}_2\text{B}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ 345 ppm acid mixture* 15 ppm tolyltriazole	0.2	35	0.20

5

* Mixture of dodecanedioic, undecanedioic and sebacic acids.

Claims

1. Method for inhibiting metal corrosion in a closed
5 water system such as is found in industrial, commercial
and institutional installations, which comprises
introducing into and maintaining in the water of such a
system, an effective amount of at least one water soluble
fatty acid salt selected from the group of salts having
10 the formulae



wherein R is straight or branched chain alkyl having
at least 6 carbon atoms or mono-, di-, or tri-hydroxyalkyl
having at least 6 carbon atoms, X is selected from the
15 group consisting of ammonium, alkylammonium, alkali
metal and amine cations, R^1 is alkyl having at least 2
carbon atoms or mono-, di-, or tri-hydroxyalkyl having at
least 2 carbon atoms and n is 2 or 3.

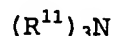
2. Method according to claim 1 wherein R is
20 straight or branched chain alkyl or mono-, di-, or tri-
hydroxyalkyl, each alkyl having from 6 to 18 carbon atoms.

3. Method according to claim 1 wherein R^1 is
straight or branched chain alkyl or mono-, di-, or tri-
hydroxyalkyl, each having from 2 to 18 carbon atoms.

25 4. Method according to claim 1 which comprises
introducing into and maintaining in the water of said
system at least one other additive selected from the group
consisting of alkali metal borates, alkali metal
molybdates, hydrocarbyl triazoles, alkali metal silicates,
30 amines and acrylic and methacrylic polymers.

5. Method according to claim 4 wherein said
amine is selected from the group consisting of ethylenedi-
amine, morpholine, pyridine and pyrrolidine.

6. Method according to claim 1 wherein X has the formula



5 wherein each R^{11} is independently selected from the group consisting of hydrogen, C_1 - C_{10} alkyl, C_2 - C_{10} hydroxyalkyl, and cycloalkyl, and when R^{11} is taken together with the nitrogen atom to which they are attached, $(R^{11})_3N$ is a heterocyclic moiety.

10 7. Method according to claim 6 wherein said heterocyclic moiety is a member selected from the group consisting of morpholino, pyridino, and pyrrolidino.

15 8. Method according to claim 1 wherein each of said salts is the same or a different member selected from the group consisting of metal salts, ammonium salts, and alkylammonium salts.

20 9. Method according to claim 1 wherein said fatty acid salt is a salt of an acid selected from the group consisting of valeric, caproic, caprylic, capric, pelargonic, heptanoic, octanoic, isovaleric, 2-ethylhexanoic, nonanoic, succinic, dodecanedioic, neodecanoic, undecanedioic, isononanoic, trialkylacetic, palmitic, stearic, malic, citric, malonic, glutaric and adipic acids.

25 10. Method according to claim 1 wherein said fatty acid salt is maintained in said system in an amount of from 1 part to about 1000 parts of said salt per about one million parts of water.

30 11. Method according to claim 1 wherein said fatty acid salt is maintained in said system in an amount of about 50 to about 525 parts of said salt per about one million parts of water.

12. Method according to claim 1 wherein said fatty acid salt is maintained in said system in an amount of about 300 parts of said salt per about one million parts of water.

5 13. Method according to claim 1 which comprises additionally maintaining in said system an effective amount of at least one member selected from the group consisting of anti-scaling agents and dispersing agents.

10 14. Method according to claim 4 which comprises maintaining said alkali metal borate in said system in an amount of about 100 to about 210 parts per million parts of water.

15 15. Method according to claim 4 which comprises maintaining said hydrocarbyl triazole in said system in an amount of about 15 parts per million parts of water.

 16. Method according to claim 4 which comprises maintaining said amine in said system in an amount of about 240 to about 300 parts per million parts of water.

20 17. Method according to claim 4 which comprises as a first step forming an aqueous concentrate comprising at least one water soluble fatty acid salt as defined in claim 1, at least one member selected from the group consisting of alkali metal borates, alkali metal molybdates, hydrocarbyl triazoles, silicates, amines, and
25 acrylates and water.

 18. Method according to claim 4 which comprises introducing into said system a mixture of salts of caproic acid, caprylic acid and capric acid, morpholine and tolyltriazole.

19. Method according to claim 4 which comprises introducing into said system a mixture of the salts of caproic acid, caprylic acid and capric acid, sodium borate
5 and tolyltriazole.

20. Method according to claim 4 which comprises introducing into said system a mixture of the salt of pelargonic acid, morpholine and tolyltriazole.

21. Method according to claim 4 which comprises
10 introducing into said system a mixture of the salt of heptanoic acid, morpholine and tolyltriazole.

22. Method according to claim 4 which comprises introducing into said system a mixture of the salts of sebacic acid and isononanoic acid, morpholine and
15 triazole.

23. Method according to claim 4 which comprises introducing into said system a mixture of the salt of tartaric acid, morpholine and tolyltriazole.

24. Method according to claim 4 which comprises
20 introducing into said system a mixture of the salts of tartaric acid, caproic acid, caprylic acid and capric acid, morpholine and tolyltriazole.

25. Method according to claim 4 which comprises introducing into said system a mixture of morpholine, a
25 mixture of neodecanedioic acids having 9 to 13 carbon atoms and tolyltriazole.

26. Method according to claim 4 which comprises introducing into said system a mixture of $\text{Na}_2\text{B}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$, a mixture of decanedioic, undecanedioic and sebacic acids
30 and tolyltriazole.

27. Method according to claim 4 which comprises introducing into said system a mixture of the salts of

neodecanoic acids having from 9 to 13 carbon atoms, the salt of sebacic acid, morpholine and tolyltriazole.

28. Method according to claim 4 which comprises introducing into said system a mixture of the salts of neodecanoic acids having primarily 10 carbon atoms, the salt of sebacic acid, morpholine and tolyltriazole.

29. Method according to claim 4 which comprises introducing into said system an amount of fatty acid salt sufficient to provide a concentration of about 1 to about 1000 ppm of said fatty acid salt per one million parts of water and of said additive of about 15 to about 500 parts per one million parts of water.

30. A concentrate for inhibiting metal corrosion in a closed water system such as is found in industrial, commercial and institutional installations having a concentration of a fatty acid salt as defined in claim 1 sufficient to provide about 50 to about 500 parts of said salt per one million parts of water in said system and from about 15 to about 500 parts per million parts of water in said system of at least one additive selected from the group consisting of alkali metal borates, alkali metal molybdates, hydrocarbyl triazoles, alkali metal silicates, amines and polymeric dispersants, in water.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/06158

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C23F11/12 C23F11/08 C23F11/10 C23F11/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C23F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

5 August 1996

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

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INTERNATIONAL SEARCH REPORT

Int. onal Application No
PCT/US 96/06158

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information on patent family members

Int. Application No

PCT/US 96/06158

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